After his return, at the age of 32, Gibbs was appointed Professor of Mathematical Physics in Yale College. At 34 (1873), he published two papers on "Graphical Thermodynamics" in the Transactions of the Connecticut Academy of Arts and Sciences. A third paper, "Heterogeneous Equilibria," was published in two parts in 1875 and 1878. At 63, Gibbs published a book written specially for the Yale Bicentennial (1901). It was a unique contribution to classical physical science in that it related continuum thermodynamics to kinetic theory; despite the subsequent development of quantum theory it still remains the statistical mechanics foundation for so-called rational thermodynamics.

On April 28, 1902, Gibbs died. He was buried in Grove St. Cemetery near his home and office.

Though Gibbs was elected in 1879 to the National Academy of Sciences, he was never a member of the American Physical Society or of the American Chemical Society, and he joined the American Mathematical Society only shortly before his death. On April 1, 1900, however, Charles Walcott, President of the Washington Academy of Sciences, wrote to H. E. Hadley at Yale to urge him to encourage acceptance by eight Yale faculty recently elected to the Washington society. Gibbs accepted; he was a member of the Washington Academy of Science, hence this occasion to commemorate the centennial of his epoch-making thermodynamics.

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# A Geometrical Description of Critical Phenomena

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ABSTRACT

Gibbs made extensive use of geometrical concepts in his development of thermodynamics. In this talk we examine the use of geometrical ideas to clarify our understanding of the thermodynamics of fluids in the vicinity of the critical point. The influence of Gibbs on recent developments in the study of critical phenomena is emphasized.

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The study of thermodynamics described in Gibbs' three papers is a rich source of information and insight for the contemporary student.[1] Today I want to focus our attention on Gibbs' use of the geometrical features of thermodynamics in his development of the mathematical structure of the theory. He began with the formulation embodied in eqs. (1) and (2) (*vide infra*) and went on to develop thermodynamics to the point where it is not conceptually distinguishable from presentations found in current texts. After we have examined Gibbs' use of geometrical relationships in formulating thermodynamics, we shall see how the use of geometry has aided our understanding of the unusual thermodynamic properties observed in the vicinity of the liquid-vapor critical point.

Let us begin by briefly considering the content of Gibbs' three papers. The first

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[1]Gibbs' work on thermodynamics is reprinted in *The Scientific Papers of J. Willard Gibbs, Vol. 1,* Thermodynamics. Dover Publications Inc., New York (1961). This, in turn, is a reprint of the volume originally published by Longmans, Green and Co. in 1906, 3 years after Gibbs died.

paper, published in 1873, considers various 2-dimensional representations of thermodynamic properties. P-V diagrams were in common use at that time, and he explored alternative ways of representing thermodynamics. In addition to showing that T-S diagrams have useful properties, he also investigated other possibile combinations of thermodynamic variables and some of the properties of such diagrams.

Later in 1873 he published a second paper on the use of surfaces to represent thermodynamics. By that time the experiments of Andrews on critical phenomena in $CO_2$ had stimulated Thompson to suggest that a PVT surface would be a useful way of representing thermal properties. Gibbs in a footnote (as frequently occurs in his work) takes note of Thompson's work and points out that the surfaces Gibbs is considering have a much greater information content than do Thompson's. The sort of surface Thompson has in mind is shown in Fig. 1. This is the familiar PVT surface which represents observations of properties faithfully but does not convey the essence of thermodynamics. Gibbs was proposing instead to use a surface representing the entropy, energy and volume of the fluid from which the equation of state can be obtained by differentiation. That is, the

energy U is a function of the entropy S and the volume V subject to the condition

$$dU = TdS - PdV \qquad (1)$$

He then proceeded using eq. (1) and the by then known condition for thermodynamic stability

$$(\delta S)_U \leq 0 \qquad (2)$$

to deduce the convexity properties of the U (S,V) surface. Again in a footnote the conditions for the equilibrium among different parts of the system are stated. These conditions are that the temperature, pressure, and what we now know as the chemical potential be uniform throughout the system.

In his third and major paper on thermodynamics, 1876–1878, the subject is explored and set out in a very elegant and complete way. The ideas in the footnotes in his second paper are (among many others) expanded and applied to a variety of interesting situations. For the purpose of the discussion at hand I want to focus on the quantity now known as the Gibbs free energy and the property that the chemical potentials (Gibbs free energy per unit mass) for phases in thermodynamic equilibrium are equal. The type of surface that results is shown in Fig. 2.

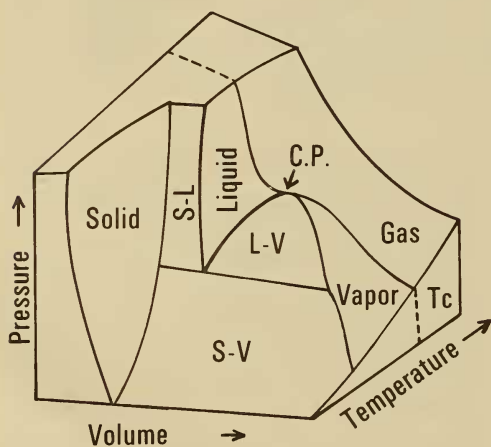The advertised topic of this talk is critical phenomena. For one-component



Fig. 1. A pressure-volume-temperature surface for a substance which contracts on freezing. The critical point (C.P.) and the critical isotherm ($T_c$) are indicated.
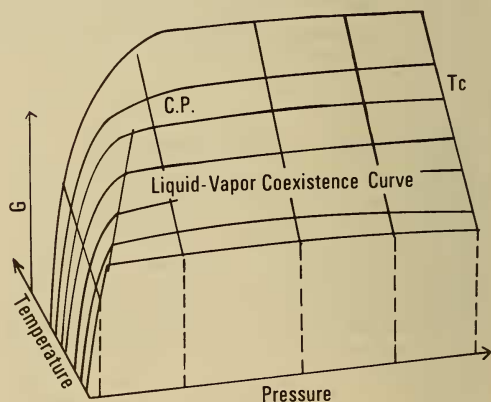


Fig. 2. A portion of a Gibbs free energy (G) pressure (P) temperature (T) surface in the vicinity of the critical point (C.P.). The critical isotherm ($T_c$) and the liquid-vapor coexistence curve are noted.

fluids the critical point is the point where distinction between liquid and gas vanishes. It is indicated in Fig. 1 at the top of the liquid-gas dome. Gibbs realized that the critical point is characterized by a horizontal isotherm with 0 curvature. It is displayed in Fig. 1 as the critical isotherm $T_c$. The critical point can be characterized by the conditions

$$\left( \frac{\partial P}{\partial V} \right)_T = 0, \quad \left( \frac{\partial^2 P}{\partial V^2} \right)_T = 0 \quad (3)$$

Critical phenomena is a topic which has, over the years, come and gone as a popular subject for scientific research. It has grown in interest because of its obvious significance for the study of thermodynamic properties of matter and because of its own intrinsic scientific interest. The study of critical phenomena has declined in time because of the lack of adequate experiments (which are quite difficult) and the corresponding difficulty of developing useful theory. During the 1950's and early 1960's there was a renewed interest in the study of critical phenomena. This time the interest in the subject did not die out but has grown into a full-fledged, mature understanding of critical phenomena. A turning point can now be recognized as occurring in 1965 when a conference on critical phenomena was held at the National Bureau of Standards.[2]

Shortly after that conference a number of things happened which have a definite Gibbsian flavor to them. One of these was the publication of a paper by Widom[3] which analyzed the thermodynamics of the critical region in ways that had not been used before and which were consistent with the anomalous properties of thermodynamic quantities. Built into this work is the crucial idea that in some way critical phenomena are universal features of matter, independent of the specific

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[2]*Critical Phenomena*, Proceedings of a Conference; Editors: M. S. Green and J. V. Sengers. U. S. Government Printing Office, Washington, D. C. 20234, (1966). NBS Misc. Publication 273.
[3]B. Widom, J. Chem. Phys. 43, 3898 (1965).

fluid in question.

Now what are the significant features of thermodynamic properties in the vicinity of the critical point? They can be characterized by divergences in the isothermal compressibility

$$K_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \sim (T - T_c)^{-\gamma}, \quad (4)$$

$$\gamma \simeq 1.2$$

in the specific heat at constant pressure

$$C_P = \left( \frac{\partial U}{\partial T} \right)_P \sim (T - T_c)^{-\gamma} \quad (5)$$

and in the specific heat at constant volume

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \sim (T - T_c)^{-\alpha}, \quad (6)$$

$$\alpha \sim 0.1$$

The topic we wish to pursue is the understanding of these anomalies from an essentially geometrical point of view. The Gibbs free energy-pressure-temperature surface, Fig. 2, can be characterized mathematically as

$$dG = -SdT + VdP,$$
$$(\delta G)_{P,T} \geq 0 \quad (7)$$

The only striking feature of this surface is the ridge representing the liquid-vapor coexistence curve. The approach to the critical point is characterized by having this ridge become less and less pronounced and finally vanishing at the critical point.

This can be envisioned by taking a sheet of paper and cutting a pie-shaped wedge out of it as indicated in Fig. 3. Take the sheet of paper and fold the cut-off wedge so that the edges touch. Then note at the point of the wedge that the curvature is different depending on whether one goes along the line which is the extension of the cut or whether one goes at some other angle. The strong and weak divergences observed in the compressibility and in the heat capacities reflect the different curvatures in the Gibbs
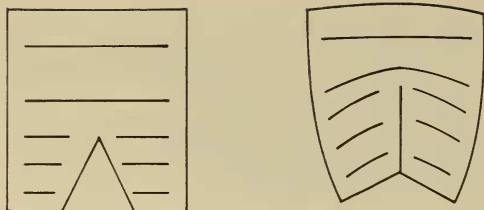
Fig. 3. A rough model of the Gibbs free energy surface can be made by cutting and folding a sheet of paper as indicated. The straight lines on the flat sheet of paper become curved when the sheet is folded.

free energy surface in the vicinity of the critical point, and *that is the essence of the geometrical characterization of the anomalies occurring in the critical region*. This concept was set forth in a thermodynamic theory of critical phenomena by Griffiths and Wheeler in a 1970 paper.[4] The theory, which is geometric in flavor, makes use of the properties of the Gibbs free energy surface in a definitely Gibbsian way to elucidate the thermodynamics of the critical region and to predict how multicomponent critical phenomena will (and apparently do) manifest themselves.

There are two essential features of this theory. The first is the idea of universality; that is that the shape of the Gibbs free energy surface near the critical point is independent of the substance. The second feature is that there is only one "direction" of any significance, that of the coexistence curve. The curvature along an extension of the coexistence curve characterizes the weak divergence observed in the specific heat at constant volume, while the curvatures associated with other directions characterize the strong divergence observed in the isothermal compressibility and the specific heat at constant pressure. These ideas lend themselves to a geometric view of multi-component critical phenomena with predictions which appear to be borne out with experiment, the ultimate test of any theory.

In summary, Gibbs was able to develop thermodynamics from a set of tentative empirical statements into a full-fledged, mathematically sophisticated physical theory through the insights gained through the geometrical considerations which he employed so skillfully. In recent times this geometrical viewpoint, when applied to the problem of the properties of matter near critical points, has been invaluable in sorting out and clarifying the many observations of anomalous properties. This is an outcome which would not have surprised Gibbs in the least, and I am sure it would have pleased him.

[4]R. B. Griffiths and J. C. Wheeler, Phys. Rev. A, **2**, 1047 (1970).